Plasma Surface Modification of Polymer Powders with Application to Thermal Energy Storage

IN-HOUNG LOH, *Department of Materials Science and Engineering,* R. E. COHEN and R. F. BADDOUR, *Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139*

Synopsis

The rotating bed plasma reactor described here permits uniform surface modification of relatively large amounts of powder materials. Scale-up to even larger batches of solids appears to be feasible. Some preliminary experimental data on the plasma surface modification of polymer powders have been presented. The results show that the flow rate, time of treatment, and type of feed gas are important operating parameters which influence the final surface character. One particular application of plasma-modified polymer powders was explored; by crosslinking and/or chemically modifying only the outermost surface regions of these powders, various polymeric materials may be rendered useful for use in thermal storage slurries. The major advantage of the surface-modified plasma treated powders over the bulk-modified powders used previously is the retention of essentially all of the pristine polymer heat of fusion in the surface-modified materials.

INTRODUCTION

Treatment of polymer surfaces with reactive and non reactive cold plasmas has received widespread attention in recent years, and several books and review articles have been devoted to this subject.[1-6] Much of the research on polymer surface modification has been focused on polymeric films or other preformed shapes, with relatively little attention devoted to plasma treatment of powders.[7,8]

In a conventional static plasma reactor, only the exposed surface of the material can be modified. Variations in the diffusion of plasma species into the voids of a static bed of powder during the progress of the reaction may result in inhomogeneous surface treatment. Intimate mixing between the powder solids and the excited gas phase should increase both the rate of reaction and the homogeneity of the surface treatment. For this purpose, plasma-fluidized bed techniques have been investigated.[8-10] Because typical cold plasma reactions on polymers are restricted in system pressure to below 1 to 2 torr, the use of the plasma-fluidized bed reaction has only been moderately successful. In the fluidized bed reaction of Anand,[8] only 2 g of polyethylene powder could be treated. Another plasma fluidized reactor has been developed with the capability of processing 1–10 g of powder materials.[9]

Bosisio et al.[11] have designed a "large volume microwave plasma generator" (LMP). This LMP assembly, which employs a tubular tumbling reactor coupled to a microwave energy source, has been used to treat batch quantities of 3–5 g of powdered solid (either mica or ground wood). Recently, Schreiber et al.[12] reported treatment of 30 g of filler using the LMP reactor.

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With the exception of this LMP assembly, we know of no other reported studies of rotating bed plasma reactors to treat relatively large amounts of powder materials.

The purpose of this paper is to report on our efforts to plasma modify 30–50-g batches of polymer powders using a newly developed rotating bed plasma reactor. We also report on the potential of some of these plasma-treated polymeric powders for use in concentrated slurries for thermal energy storage applications.

DESCRIPTION OF APPARATUS

The overall setup for our rotating bed plasma reactor is shown schematically in Figure 1. It consists of a 13.56-MHz rf generator (LFE Corp.), a tubular reactor with rotating vacuum seals, an auxiliary setup for monitoring and controlling gas stream flow rates and reactor pressure, a downstream mass spectrometer for analysis of gas phase species, and an emission spectrometer for analyzing the energetics of the glow discharge.

Reactant gases enter through mass flowmeters (Hasting-Raydist, Model Nall 100 and LF 50) and micrometer needle valves (Nupro), and then admitted into the plasma reactor. The exhaust gas pass through a liquid nitrogen trap and then to the vacuum pump (Sargent Welch, Model 1402). The system pressure is regulated by constricting the downstream vacuum valves (Varian, Model 1251-3/4) and is monitored by an absolute capacitance manometer (MKS Baraton, Model 221A) before and after the reactor.

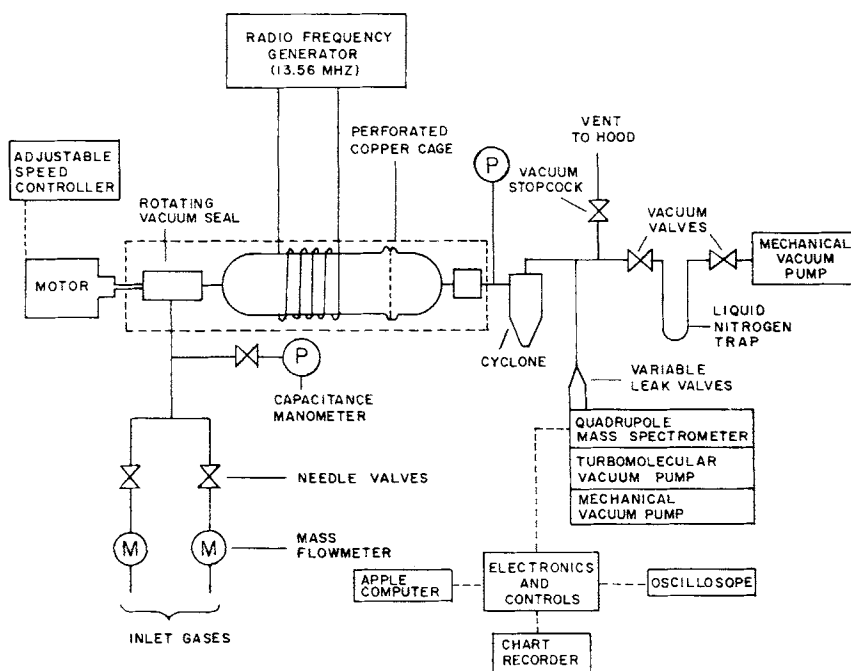The tubular reactor with rotating vacuum seals is the key component of

Fig. 1. Reaction system with rotating bed plasma reactor.

the rotating bed plasma reactor; a detail is shown in Figure 2. The reactor is made of Pyrex, 8 cm in diameter, and is separated into two parts, 27 cm and 6 cm long, respectively. This separation allows for ease of sample loading. The rotating vacuum seals are constructed of brass, Teflon and Nylon (modified versions of ACE Glass, Model B6714-04). The modifications include a hollow glass tube with one end attached to the reactor and two holes drilled near the center through which the reactant gases enter. The reactor is rotated by a variable speed gear motor (Bodine, Model 42D 5BEPM-53) with a variable speed control (Minarik Model SLF68). The rotation speed of the reactor varies in the range of 2–50 rpm. In order to enhance the contact of the plasma with the particle surfaces, a bafflelike structure was constructed by dimpling the reactor wall at several points around its periphery.

All upstream tubing is 0.25 in. copper or flexible stainless steel (Cajon); downstream tubing is 0.75 in. copper or flexible stainless steel. Connections are made using either Swagelock or Cajon vacuum connectors. A grounded, perforated (0.25 in. diameter holes) copper box completely encloses the plasma reactor, except for the entry and exit points of the gas flow system. This copper box shields the electronic equipment from radio frequency interference. The tubular reactor was inductively coupled to the radio frequency power supply (LFE Corp., Model SA-40-C) via a would copper coil. Shielded coaxial cable (Belden 8237, 50 Ω) was used to transmit power from the generator to the coil. A matching network with auto-tunner construction minimized the reflected power to protect the generator. A UV-Visible (200 to 800 nm) emission spectrometer (Instruments SA, Model H-20UV-V) was used to analyze the plasma components. A quadrupole mass spectrometer (VG, Model Spectralab 200) capable of analyzing the mass range from 1 to 200 amu was located downstream to sample the stable effluent gaseous species. The detailed constructions of these components were described by Corbin.[13]

EXPERIMENTAL

Polymer powders were obtained from commercial sources and no further purification was performed. The high density polyethylene (HDPE) powder (free of additives, 8.0 melt index, relatively narrow molecular weight distribution and 0.965 g/cc density) was obtained from Union Carbide. The polyacetal (POM) and Nylon pellets were purchased from Scientific Polymer Products, Inc.; polypropylene (iso PP) powder was purchased from Polyscience Inc.
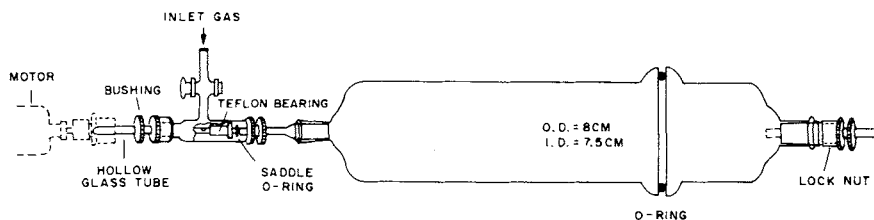

Fig. 2. Rotating Reactor, detail.

In a typical run, polymer powders (or pellets) were placed inside the reactor prior to evacuation. When the pressure dropped to less than 0.1 torr, the reacting gas was admitted and allowed to flow for approximately 10 min before turning on the plasma. The powders were tumbled inside the reactor at a rotation speed of 4 rpm. The pressure, as monitored by the capacitance manometers, was on the order of 1 torr. Power supplied to the reactor was 20 W in all cases. Using these treatment conditions, the temperature at the powder surface was not over 50°C.[13,14] The reactions were carried out with different gases and gas mixtures, flow rates, and reaction times. Reacting gases included helium, 5% fluorine in helium and 10% CF_4 (Freon-14) in helium. At the end of the reaction the rf power was turned off and the reactor was flushed with helium gas at 1 torr for 10 min. Finally helium was slowly (over a 10-min period) leaked in to bring the reactor up to atmospheric pressure before the powders were removed.

Surface compositions were investigated by X-ray Photoelectron Spectroscopy (Physical Electronics Industries Inc.) with the use of $MgK_{1,2}$ radiation (1253.6 eV). The powders were carefully and lightly dusted onto double-stick tape, which was then mounted on a glass cover slide for analysis. During acquisition of the data, there was a buildup of surface potential for the nonconducting powder samples. Therefore, the gold-decoration and charge neutralization technique[15] was utilized to obtain reproducible high resolution spectra. The surface groups CF/CHF, CF_2 and CF_3, which possess chemical shifts from the main Cls peak of 4.7, 6.7, and 9.0 eV, respectively,[16] were used to identify the degree of fluorination, as in previous work on polymer films.[8,10,13,16] A Mettler DSC-2000 differential scanning calorimeter was employed for examining in the thermal behavior of the plasma-treated polymer powders.

RESULTS AND DISCUSSION

Flow rate, time of treatment, and type of gas are parameters which are known to influence the surface treatment of polymer films.[8,10,13] The importance of these parameters has been reconfirmed here for the powder materials. The effects of these parameters are reported here in terms of high and low resolution ESCA spectra. The surface atomic ratios reported below are obtained by area measurements of different ls sub-peaks seen in the high resolution spectra.

ESCA survey spectra (low resolution between 1000 and 0 eV) are shown in Figure 3 for HDPE powder before and after plasma fluorination. The large fluorine ls peak appearing near 700 eV indicates that extensive fluorination has occurred. In the high resolution mode, the ESCA spectra reveal shifts of the C(ls) peaks resulting from changes in the chemical environment of the carbon atom. Figure 4 shows a representative high resolution carbon ls spectrum for the fluorinated HDPE powders. Five different peaks are identified. These peaks can be labelled in Figure 4 as ($-CF_3-$), ($-CF_2-$), (CF— or CHF—), ($-CH_2-CF_x-$, or $-CO-$), and ($-CH_2-CH_2-$). The fluorinated HDPE powder is compared to fluorinated HDPE film in Figure 5. These two materials have the same surface F/C atomic ratio, and the shape of the carbon ls ESCA spectrum is similar. This similarity suggests
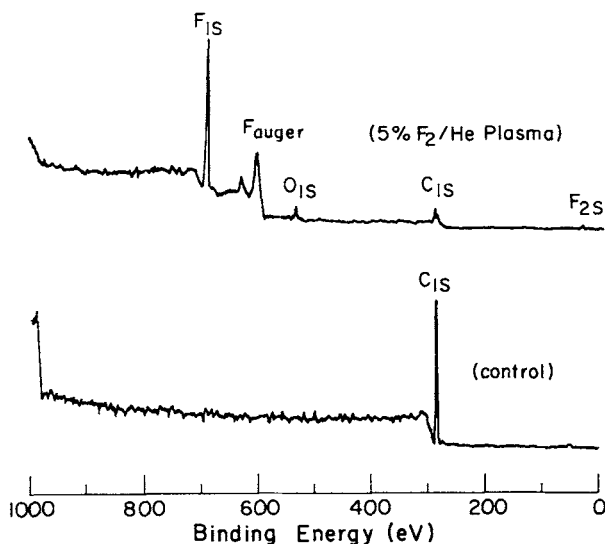
Fig. 3.   ESCA survey spectra of plasma fluorinated high density polyethylene powder.

that the same chemical structures appear on the treated particle surface and film surface, leading confidence to the efficacy of the rotating bed reactor system.

The effect of gas flow rate on the extent of fluorination of HDPE powder is depicted in Figure 6. The highest flow rate of 42 sccm leads to largest observed degree of fluorination. An explanation for this phenomena has been put forth by Clark and Dilks[17]; increased flow rate results in a greater efficiency in the removal of volatile reaction products such as H_2 and HF, which tends to increase the conversion of the surface toward a perfluorinated product.

The influence of reaction time on the degree of fluorination and the atomic percent of oxygen is shown in Figure 7. The extent of the fluorination reaches a maximum at approximately 60 min. It is known from previous work that ablation and reaction occur simultaneously in the glow environment.[8,13] These two parameters apparently reach a steady state after approximately 60 min of reaction, since higher degrees of fluorination are not observed at longer times. The surface oxygen content decreases as the re-
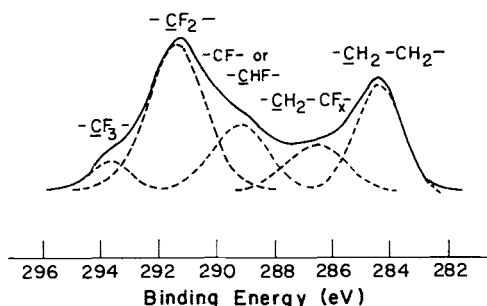

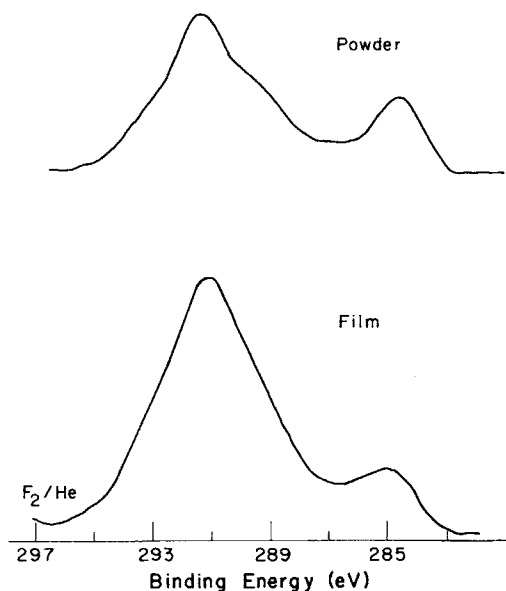Fig. 4.   ESCA Cls spectrum of plasma fluorinated high density polyethylene powder.

Fig. 5.   ESCA Cls spectrum of plasma fluorinated high density polyethylene film powder.

action proceeds. This was also observed by Anand.[8] The presence of the oxygen has been explained by the impurities in the feed gas, atmospheric leaks in the vacuum system, and etching of the reactor wall. Most of the oxygen impurities react with the polymer surface in the early stages of the reaction and are subsequently etched away as the ablation process proceeds.

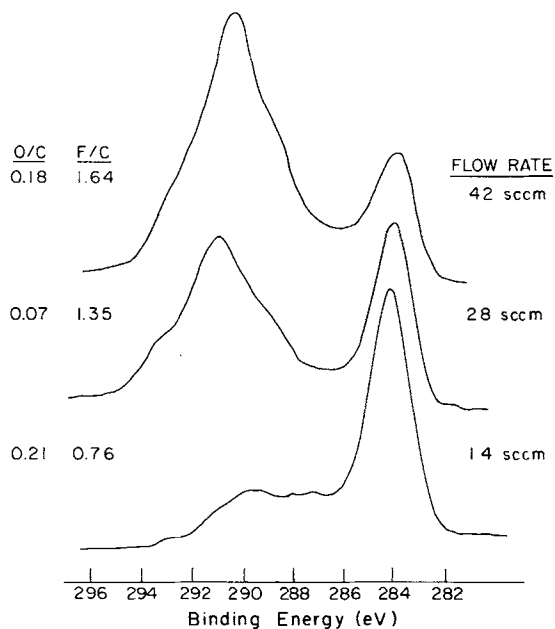HDPE powders treated with a helium plasma were also examined. The

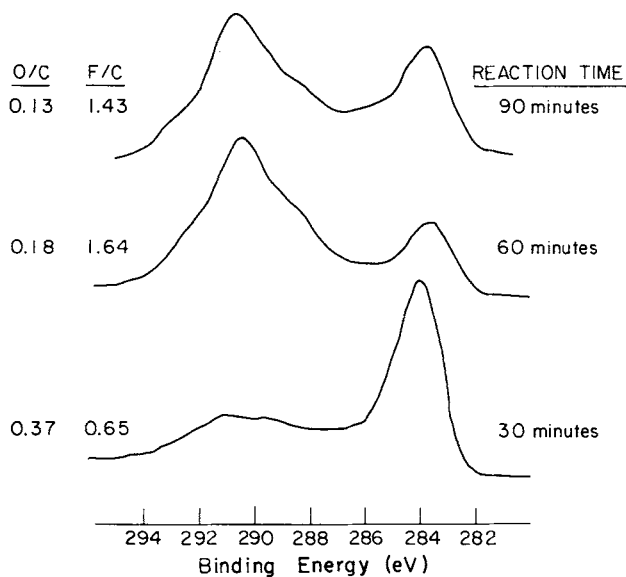Fig. 6.   Variation of the Cls spectrum with reaction time.

O/C   F/C   REACTION TIME
0.13   1.43   90 minutes

0.18   1.64   60 minutes

0.37   0.65   30 minutes

294 292 290 288 286 284 282
Binding   Energy (eV)

Fig. 7. Variation of the C1s spectrum with flow rate.

ESCA spectrum of this material indicates that, except for a small percentage of oxygen which exists on the surface, the chemical composition is the same as for nontreated materials.

DSC (10 K/min) of the various plasma treated polymer powders showed no change in the melting point and degree of crystallinity, and did not reveal any significant features in the thermograms attributable to the surface modifications (Table I). This suggests that the bulk properties of the powder materials have not been changed by the plasma process, which is similar to previous findings.[8] Because the fluorinated layer is expected to be less than about 100 nm in thickness[8,11,13] and the powder particle sizes were always larger than 10^5 nm, the lack of influence of the surface modification on the bulk thermal behavior is not unexpected.

One of the fluorine-treated HDPE powders (F/C = 1.0) was molded into films at 145°C and 3 MPa pressure. The ESCA spectrum of this molded film showed only 6.7% of fluorine on the surface. The decrease in surface fluorine content indicates that the molding process squeezes out the molten non-

TABLE I
Thermal Properties of Plasma Treated Polymer Powders

Polymer	Plasma	Crystallinity	mp (°C)	H_f (cal/g)
HDPE	Control	80%	134	56
HDPE	He Plasma	79%	133	54
HDPE	F2/He Plasma	83%	133	58
Nylon 6,6	Control	41%	261	83
Nylon 6,6	F2/Ar Plasma	40%	262	80
Iso PP	Control	53%	160	100
Iso PP	F2/Ar Plasma	54%	159	99
POM	Control	71%	179	178
POM	F2/Ar Plasma	74%	175	185

fluorinated polymer which then comprises the continuous phase of the final molded film.

APPLICATION: THERMAL ENERGY STORAGE

Certain polymeric materials have been examined in terms of their potential for thermal energy storage (TES) for home[18] and industrial[14] heating and cooling operations. The most attractive candidate material is a lightly crosslinked high density polyethylene in the form of pellets; the crosslinking is necessary to prevent the pellets from sticking together when heated above the melting point.

Three methods of controlled chemical crosslinking of HDPE have been reported[18]: (i) peroxide-initiated, free radical crosslinking, (ii) vinyl triethoxy silane grafting and crosslinking, and (iii) electron beam crosslinking. In all of these cases, the crosslinks eliminate the melt flow (desirable for high-temperature form stability) but they decrease crystallinity and heat of fusion (undesirable for TES). All three methods of crosslinking have been reported to result in losses 20–30% of the initial heat of fusion.[14,18]

In this work, we wished to determine whether plasma surface chemical modification and/or surface crosslinking could be successful in producing thermally stable polymer powders (or pellets) while retaining essentially 100% of the initial heat of fusion of the original polymer. Several commercial polymers with high percentages of crystallinity and covering a range of melting points were studied to determine possible candidates for use as thermal energy storage materials. Samples of polymer powder or pellets (30–50 g) were plasma-treated utilizing the rotating bed reactor described above. The three feed gases employed in these experiments were 5% F_2He, 5% F_2/95% Ar, and He.

The TES properties of the plasma treated powders were tested by mixing the polymer powders with either ethylene glycol or silicone oil and heating to temperatures above their melting points. The samples were then allowed to cool to room temperature. Five melt/cool cycles were employed; the results are summarized in outline form in Table II. Heat of fusion measurements (DSC) were conducted using a heating rate of 10°C/min. The results of those tests have already been reported in Table I above.

As shown in Table II, both the details of the plasma treatment conditions and the nature of the precursor polymer play a major role in the development of a thermally form-stable TES material. It has generally been observed that exposure of polymers to an activated inert gas plasma results in extensive crosslinking on the polymer surface layer.[19,20] Both the ultraviolet radiation and reactive radicals in the plasma are capable of generating free radicals on the surfaces of many polymers which lead to the formation of crosslinks in the outermost surface. It is important that the thickness and integrity of the crosslinked layer to be large enough to retain the melt polymer within its shell when the temperature is raised above the melting point. Development of a surface crosslinked layer has been shown to be related to the length of plasma exposure, the choice the plasma conditions and the nature of the polymer.[21,22] Table II shows that both the fluorine plasma- and helium plasma-treated high density polyethylene would be good TES materials, but that similarly treated isotactic polypro-

TABLE II
Characterization of Plasma-Treated Polymer Powders

Polymers	Treating conditions	Form-stability in fluid	Rating
HDPE	None (control	Powders totally fused together at 132°C	Unsuitable for TES
HDPE	He plasma, low flow rate	Powders adhere slightly at 135°C, but break apart when cooled	Not good for TES
HDPE	He plasma high flow rate	Powders very firm, no tendency to self-adhere at all up to 145°C	Excellent for TES
HDPE	F2/He plasma, CF4/He plasms	Powders very firm, no tendency to self-adhere at all up to 145°C	Excellent
Iso–PP	None (control)	Powders fused together at 160°C	Unsuitable for TES
Iso-PP	He plasma	Powders fused together at 160°C	Unsuitable for TES
Iso-PP	F2/ He plasma, F2/ Ar plasma	Powders totally fused together at 160°C	
Iso–PP	F2/He plasma, F2/ Ar plasma	Powders totally fused together at 160°C	Unsuitable for TES
P(OM)	None (control)	Powders fused together at 180°C	Unsuitable for TES
P(OM)	F2/Ar plasma	Powders fused together at 180°C	Unsuitable for TES

pylene would not. This observation can be explained by postulating a different degree of crosslinking on the surface for these two cases. Hall et al.[22] have shown that polyethylene surfaces can be crosslinked by helium or oxygen plasmas; however, polypropylene has been successfully crosslinked by oxygen plasmas but not by helium plasma.[23] Further research is underway to determine the most suitable plasma modification conditions for surface crosslinking other candidate polymers for TES applications.

It is clear from the results reported here that plasma-surface-modified HDPE may be an excellent candidate material for TES applications. The visual observations of the melt/cool cycles of dense slurries of the surface treated HDPE in ethylene glycol are remarkable. In a narrow (1 or 2°C) temperature range near the melting point, the slurry transforms from a white opaque medium below T_m to a transparent suspension of tiny deformable droplets above T_m. This phenomenon is entirely reversible over an apparently unlimited number of cycles. Many interesting applications of such nonadhering powdered polymer slurries can be envisioned, including their use in rheological experiments to determine the effect of particle deformability on the viscosity of concentrated suspensions.

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